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(54) PROTECTIVE PROCESS FOR FERROUS AND NON-FERROUS METAL SURFACES AGAINST CORROSION BY CARBURATION AT HIGH TEMPERATURES AND CORROSION BY OXIDATION

(71) We, MONTEDISON S.p.A., of 31 Foro Buonaparte, Milan, Italy, an Italian Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

This invention relates to a process and a coating composition for the protection of ferrous and non-ferrous metal surfaces against corrosion by carburation at high temperatures which may or may not occur simultaneously with corrosion phenomena by oxidation.

An example of corrosion through carburation at a high temperature is that in the piston heads of large Diesel engines, which come into contact with carbonaceous incrustations, notwithstanding the presence of oxygen that is injected in order to achieve combustion.

As is known, corrosion phenomena of this type often lead to the breaking through of the piston heads or at least such damage as to put the piston itself out of service.

Another example is given by installations for the production of hydrogen by cracking of methane or other hydrocarbons or mixtures thereof. Another case of corrosion through carburation is given by plants for the production of ethylene through cracking of hydrocarbons.

In this case the production of the ethylene takes place inside metal tubes used as reactors. Such tubes must work at a temperature of about 1000°C and must resist the chemical attack developed by the carbon black (originating as a noxious by-product following heterogeneous catalytic phenomena induced by the metals of the wall, in particular by nickel) on the hot wall of the tube itself where it is converted to coke.

In fact, in consequence of this chemical attack, the tube carburates itself, not only on the inner surface but also inside the metal wall itself, wherein the carbon diffuses more or less deeply.

Since the carbon black accumulates on the wall as coke as the reaction proceeds, hindering the transmission of heat (which is fed in from the outside to balance the endothermicity of the ethylene producing reaction), it is necessary to periodically interrupt the production of the installation. This interruption allows the carrying out of "decoking", by which the reactors are freed from the deposits of carbon black. This cleaning is obtained by burning the carbon black through the immission of air into the reactor together with steam.

The alternate conditions of carburation (in the ethylene production phase) and of oxidation (in the decoking phase) are the cause of the deterioration by intergranular corrosion of the tubes, corrosion that, at the mechanical and thermal stresses under which the tubes are operating, causes the rupture of these latter.

Austenitic stainless steel, unable to withstand such severe operational conditions, has been replaced by special austenitic alloys obtained by centrifugal casting.

Nowadays, the most diffusely used material is the HK-40 alloy which offers the best compromise between cost and duration.

However, this alloy which offers satisfactory results for temperatures not exceeding 950°C, shows a rapid deterioriation of the resistance characteristics as soon as the temperature attains a value comprised between 1000° and 1100°C.

All installations would tend to operate at this more boosted level, if there was not the obstacle of the failing resistance, since at such a level the yield of the reaction would rise considerably (+40%, when passing from 1000°C to 1100°C).

The present invention in one aspect provides a process for the protection of ferrous and non-ferrous metal surfaces against corrosion by carburation at high temperatures and corrosion by oxidation, the process comprising : preparing a binary or polynary mixture of fine powdered product having a particle size from 0.04 to 0.00004 mm, the mixture comprising at least one first component selected from Si, Si_3N_4, $ZrSiO_4$, SiC, SiO_2, glass, clay, Fe-Si, Al_2O_3, ZrO_2, MgO, WO_3, Cr_2O_3, Cr_3C_2 and Cr, the or each said first component being present in an amount of from 0.5 to 92% by weight, and the total amount of the said first components not exceeding 99.5% by weight, and from 0.5 to 50% by weight of at least one second component selected from AlB_2, AlB_{12}, Al-stearate, Al, Cr-Al, B_2O_3, B_4C, Fe_2O_3, TiB_2, ZrB_2, Fe and Fe-Cr; dispersing the said mixture in a liquid medium acting as a binder, in such a quantity as to obtain a composition suitable for painting of the desired density, the said liquid medium being an aqueous or an organic liquid; mechanically homogenizing the composition, and then painting or coating a metal surface of a product to be protected, the surface having been preliminarily sand-blasted or chemically cleaned; drying the coating product, first in the air at room temperature, and then at a temperature higher than room temperature; and finally baking the coating at a temperature not lower than 700°C in an oxidizing atmosphere.

The invention in another aspect provides a coating composition for protecting ferrous and non-ferrous metal surfaces against corrosion by carburation at high temperatures and corrosion by oxidation, the composition comprising : a binary or polynary mixture of fine powdered product having a particle size from 0.04 to 0.00004 mm, the mixture comprising at least one first component selected from Si, Si_3N_4, $ZrSiO_4$, SiC, SiO_2, glass, clay, Fe-Si, Al_2O_3, ZrO_2, MgO, WO_3, Cr_2O_3, Cr_3C_2 and Cr, the or each said first component being present in an amount of from 0.5 to 92% by weight, and the total amount of the said first components not exceeding 99.5% by weight, and from 0.5 to 50% by weight of at least one second component selected from AlB_2, AlB_{12}, Al-stearate, Al, Cr-Al, B_2O_3, B_4C, Fe_2O_3, TiB_2, ZrB_2, Fe and Fe-Cr; the mixture being dispersed in a liquid medium acting as a binder so as to obtain a composition suitable for painting, the said liquid medium being an aqueous or an organic liquid.

As a dispersing liquid there is preferably used a silicone containing organic liquid and, before applying the paint, the metal surface is preferably coated with a bonding layer consisting of nickel-boron deposited by an electroless sodium boranate chemical process or, alternatively, consisting of chromium deposited by the molten-spray process.

More particularly, the protective process of the invention is in practice preferably carried out according to the procedures indicated in detail as follows.

The powders of the materials used have a size of from 0.004 to 0.00004 mm. The powders with such a size are obtainable either by grinding of commercially available materials, or by direct preparation in a plasma-reactor.

The powders are products belonging to the class of metals, of metal-ceramics and of ceramics. The powders are subdivided into a first group of components (comprising: Si, Si_3N_4, $ZrSiO_4$, SiC, SiO_2, glass, clay, Fe-Si, Al_2O_3, ZrO_2, MgO, WO_3, Cr_2O_3, Cr_3C_2, and Cr) and a second group of components (comprising: AlB_2, AlB_{12}, Al-stearate, Al, Cr-Al, B_2O_3, B_4C, Fe_2O_3, TiB_2, ZrB_2, Fe, Fe-Cr).

According to the invention the powders of the first group are used in the powdery mixture in concentrations such that the or each first component is present in an amount of 0.5 to 92% by weight, the total amount of the first components not exceeding 99.5% by weight, the powdery mixture further comprising from 0.5 - 50% by weight of one or more components of the second group.

The mixture of powders are added to a liquid acting as a dispersant and binder, in such a quantity as to obtain a more or less fluid consistency, suited for each single case of application.

The liquid medium used may be either of an aqueous or of a non-aqueous nature. In the latter case, the liquid will be of an organic nature, and preferably consist of from 50% to 86% by weight of one or more aromatic solvents and from 50% to 14% by weight of a silicone having a molecular weight of from 1300 to 3600. The silicone preferably has a silicon content of 14 to 37% by weight; the silicone is also soluble in the aromatic solvent used as liquid organic medium.

In the following description the dispersing medium will be indicated with the term: "silicone organic liquid".

The dispersion of the powder mixture is homogenized according to one of the various known systems that are suited for producing painting products of a good homogenization (e.g. roller refiners, vibration mills, colloidal mills).

The application of the paints is carried out according to anyone of the conventional known methods (i.e.: by brush, by spraying, by roller spreaders, by dipping, etc.). The application of the paint is in any case carried out after a chemical cleaning treatment

according to anyone of the various known systems or after a sand-blasting treatment.

The chemical cleaning or sanding treatment must be considered as pre-treatment to be carried out in any case before the application of the paint.

According to a preferred variant of this invention, after the chemical cleaning or sanding, and before the painting, there is deposited a thermoresistant metal layer with a connecting function. This metal layer, having a thickness comprised between 5 and 500 microns, may consist of nickel-boron deposited by an "electroless" sodium boronate chemical reduction process (also called sodium boronhydride - Na BH_4), or preferably of metal chromium deposited with one of the processes of the molten-spray technique (starting from powder or sticks or from flexible plastic cord).

The interposition of this metal layer improves the bond between metal base and the protective paint. The best bond may be obtained with a chromium layer, though also a nickel-boron obtained from sodium boranate may be used with satisfactory results. Metal chromium, besides having the function of a link, has also the important role of being a component of the paint which is applied with a protective purpose on the metal coating, as will be demonstrated in the examples that will follow herein-after.

The drying of the piece painted as described above is conducted in an air atmosphere at room temperature, so that the elimination of the aqueous or organic liquid removable by evaporation shall take place slowly, so as not to damage the coating layer formed by the paint. This first drying is then followed by a further drying in a dryer, so as to complete the drying until eliminating the last traces of aqueous and non-aqueous volatile substances.

The drying phase is conducted at a temperature comprised between 50° and 300°C. In the case in which the liquid used is organic silicone, the protective coating will have a greater resistance on a virgin base surface since the silicone acts as a binder.

There then allows the baking of the dried manufactured articles in a furnace at a temperature comprised between 700° and 1400°C, in an atmosphere of air, so that oxidation processes shall develop.

In the reacting system, consisting of the layer produced by the applied paint, there actually take place the local chemical transformations or conversions (or topochemical transformations) which, thanks to the oxidating medium, establish the definitive "bonding" of the components present in the protective coating. In this phase of the process the silicone, in those cases where it is present, by decomposing itself, generates finely distributed SiO_2, which contributes to the formation of the final bonding in the system.

The duration of the baking phase depends on the mass of the metal product and may last just for a few hours. Of course the number of coats of paint may be more than one, depending on the thickness of the coat one wishes to obtain from the painting product.

In the case of several coats, there may be carried out either one single baking or, alternatively, as many bakings as there have been applied coats of paint. In the case of one single baking, the number of dryings in the air shall always be equal to the number of coats of paint applied.

The manufactured product coming from the baking will be ready for use and will be capable of resisting conditions of corrosive attacks by carburation, with or without accompanying or successive phenomena or corrosion by oxidation.

The protective process is particularly applicable to the inner surface of the thermal reactor tubes of the petrolchemical industry. The process, in fact, is intended as an integral part of hydrocarbon cracking for the production of olefines and in particular of ethylene.

In fact, the protection of the inner surfaces of reactor tubes of hydrocarbon cracking furnaces producing ethylene in this way, surprisingly allows reduction of the formation of carbon black and its deposition as coke on the metal wall thanks to the modification of the mechanisms of the heterogeneous catalysis provoked by the protection itself.

The lack of or reduced formation of carbon black and its adhesion, rendered difficult on the surfaces treated with this protective process allow reduction of the formation of coke and its corrosive action on the walls, as well as the attaining of consequent advantages such as for instance: a greater output of the plant, higher operational temperatures, greater operational reliability and reduced energy requirements.

The invention will be further described with reference to the following illustrative Examples.

Example No. 1:

Starting from an AISI-304 stainless steel tube (outside Ø 33 mm, inside Ø 29 mm) there were prepared 6 cylinders 25 mm high, which were subjected singly to the following separate surface treatments:

1st cylinder: sand-blasted with metal sand.

2nd cylinder: sand-blasted with metal sand, followed by deposition by plasma-spraying (in argon) of a nickel coating of 0.1 mm thickness.

3rd cylinder: sand-blasted with metal sand, then followed by galvanic deposition of 0.15 mm of nickel.

4th cylinder: sand-blasted with metal sand, followed by chemical deposition ("electroless") of 0.015 mm of nickel, by reduction with sodium hypophosphite.

5th cylinder: sand-blasted with metal sand, followed by plasma-spray deposition (in argon) of a nickel-chromium coating (80% Ni, 20% Cr) of 0.1 mm thickness.

6th cylinder: sand-blasted with metal sand, followed by plasma-spray deposition (in argon) of a 0.1 mm thick chromium coating.

These six tubes were then subjected to a thermal treatment inside a horizontal quartz tube, for a period of 7 hours, and at the temperature of 1000°C, under a gaseous current, at a flow rate of 25 lt/hr, consisting of a mixture of 52% by volume of H_2, 34% by volume of CH_4 and of 14% by volume of CO.

After extraction of the tubes from the furnace, it was found that all of them were covered with a layer of carbon black. By a deformation by crushing test, it was found that all the small cylinders suffered rupture due to the carburation suffered by the structure which thus had lost the original plastic deformation properties. The least pronounced embrittlement was shown by the 6th cylinder.

Example No. 2:

There was prepared a liquid medium acting as a dispersant and binder for the elements composing the paints, according to the following procedure:

as a binder was used a silicone having a molecular weight of 1860 and a percentage composition by weight of:

C = 44.5% by weight; H = 5.15% by weight; Si = 27.14% by weight; O = 23.19% by weight.

As a solvent for the silicone there was used an aromatic mixture of the following composition:

Toluene	=	10.7 %
Ethylbenzene	=	13.0 %
p-xylol	=	11.8 %
m-xylol	=	26.7 %
isopropylbenzene	=	0.27%
higher aromatics	=	31.02%

The silicone solution, in the following indicated as organic silicone medium, is achieved by adding 22 parts of silicone, 78 parts of the above indicated mixture of aromatic solvents and by then bringing this mixture, under stirring, to full homogenization. The solution thus prepared was used as a dispersing and binding agent for metal ceramic or ceramic powders, in the preparation of protective paints for metal surfaces, as specified in the following examples.

Example No. 3:

This example is given in order to prove the adhesion properties to metal surfaces (AISI-304) of the coatings obtainable with protective paints.

15 different paints were prepared by mixing and fine grinding of the ceramic components and by a successive dispersion of the solid in the liquid (organic silicone medium of example 2), according to the values reported in Table 1.

The paints thus prepared were applied by brush to sand-blasted surfaces of small metal tubular cylinders of AISI-304 stainless steel (exter. Ø 33mm; inter. Ø 29 mm; h = 25 mm). The painted test pieces were placed into a muffle furnace in an air current, and kept there at 800°C for a period of 1 hour. After extraction from the muffle furnace, and after natural cooling down to room temperature, the test pieces displayed ceramic coatings (that formed themselves during the thermal treatment) of good coherence and adhesion.

TABLE 1

COMPONENTS OF THE PAINTS

Paint No.	Al_2O_3 % b.w.	B_4C % b.w.	$ZrSiO_4$ % b.w.	ZrO_2 % b.w.	TiB_2 % b.w.	MgO % b.w.	ZrB_2 % b.w.	Si_3N_4 % b.w.	Diato-mite % b.w.	SiC % b.w.	WO_3 % b.w.	ground quartz % b.w.	SiO_2 silicon % b.w.	Solid/liquid ratio by weight
1	90	10												3.0
2		10	90											3.3
3		10		90										2.7
4	90				10									3.0
5				90	10									2.7
6			90		10									3.3
7						80	20							2.4
8							10		90					1.3
9							10			90				1.3
10		10									90			1.7
11		10										90		1.6
12		10						90						2.0
13		10								90				1.2
14					10			90						1.1
15					10					90				1.0

Solid = mixture of the ceramic components
Liquid = organic silicone medium.

Example No. 4:

This example is given for proving the carbon black inhibiting property of the protective coating and the adhesion of the latter as well as its resistance properties at a temperature of 1000°C. There were prepared thirteen different paints, the greatest part in an organic silicone medium while the smaller part was in an aqueous medium, according to the compositions given in Table 2. The paints were prepared by proportioning the quantity of solid to the quantity of the dispersing liquid medium, so as to satisfy the rheologic properties of the paints themselves. For instance, to the aqueous paints (18 and 22) there were added minimum quantities of a polyacrylamide (Separan) in order to improve the film-generating properties of the paints themselves. "Separan" is a Registered Trade Mark. With said paints there were painted 13 (thirteen) ceramic nacelles of the type used for carbon or thermogravimetric analyses (8 cm long, 1 cm wide). On the central part of the nacelles there was wound a three-looped coil of copper wire and a three-looped coil of nickel-wire (∅ of the wires = 0.1 mm), both arranged on the layer of painting previously dried at 200°C.

The nacelles were then heat-treated inside a horizontal quartz tube for a period of 7 hours at 1000°C, under a gaseous current flowing at the rate of 1 lt/hr of a mixture consisting of: 52% by vol. of H_2; 34% by vol. of CH_4; 14% by vol. of CO.

On extracting the nacelles from the furnace, there was observed the presence of great quantities of carbon black only on the loops of the metal wires; the coatings generated by the paints, on the contrary, were clean and of a good hardness, adhesion and coherence.

TABLE 2

Paint No	SILICON		COMPOUNDS IN % BY WEIGHT					OTHER COMPOUNDS IN % BY WEIGHT							
	Glass (*)	Si_3N_4 (°)	Mixture of Si_3N_4 + 10% H_3BO_3 (**)	Clay	Glass (***)	SiC	Fe-Si	Al stearate	Al	Cr	Cr_3C_2	Cr_2O_3	Al_2O_3	B_4C	ZrO_2
16	10							10			40				40
17		90					5							5	
18	9.5	85.5						5							
19	8.2	73.8						3			15				
20	9.5							5					85.5		
21	9.5	38						5			47.5				
22		90			5				0.5	4.5					
23						60						30		10	
24						80								20	
25						85	10							5	
26			80				10							10	

(*) composition: 54.9% b.w. of SiO_2; 18% b.w. B_2O_3; 9.2% b.w. of Al_2O_3; 6.0% b.w. of CaO; 8.9% b.w. Na_2O

(**) preliminarily calcined in air at 800°C;

(***) composition: 55.2% b.w. of SiO_2; 11.1% b.w. B_2O_3; 0.3% b.w. PbO; 8.6% b.w. Al_2O_3; 2.7% b.w. CaO; 5.0% b.w. Na_2O

(°) the Si_3N_4 was added to the other pre-ground and pre-calcined in air at 800°C components.

N.B.: Paints 18 and 22 were dispersed in water; the other paints were dispersed in the organic silicone liquid.

Example No. 5:

This example is given in order to demonstrate the resistance properties of the paints under conditions of a higher temperature (1250°C).

The nacelles or bars of the preceeding example (except those corresponding to paints (22, 23, 24, 25 and 26), were again introduced into a Pitagorean tube and kept there for another 7 hours under the same gaseous flow of the preceeding example, with the only difference that the furnace temperature in this case was brought up to 1250°C.

On extracting the test bars from the furnace, it was noticed that all the bars displayed coatings of good hardness which becomes excellent in the case of composition 18.

On the coating of composition 16 there were present very short acicular carbon fibres; on compositions 20 and 21 there were likewise present longer acicular carbon fibres. For the other compositions the surfaces of the coatings appear free of acicular fibres. At the ends of the test bars, on the side of the downflow of the gaseous mixture, and for compositions 16, 17, 18 and 19, there could be noticed a few pyrolitic graphite stalactites.

The importance of this test is centered on the elevation of the high refractoriness of the tested coatings and of their repulsive property against the adherence of carbon black particles produced by the cracking of the hydrocarbon present in the gaseous mixture adopted as a flowing atmosphere.

Example No. 6:

The paints corresponding in their composition to nos. 16, 17, 18 and 24 of Table 2 of example 4, all dispersed in an organic silicone liquid, were applied by brush on 4 different tubular cylindrical test pieces of AISI-304 stainless steel (ex. ∅ = 33 mm; inter. ∅ 29 mm; h = 25 mm), previously sand-blasted and coated with a layer (0.1 mm) of chromium applied by plasma-spray deposition (in argon).

The cylindrical test pieces were kept for 1 hour at 800°C in an air atmosphere. They were then subjected to a carburation test as described in example 1.

On extracting the test pieces it was observed that the surfaces of the test pieces were free of carbon black deposits and that the protective coating displayed refractory properties.

In a deformation crushing test it was observed that the test pieces had preserved the specific plasticity typical for the material of the original metal material, and of not having suffered any rupture and; thus, not even carburation.

Example No. 7:

This example is given to illustrate the function of the chromium, which not only functions as a connecting basic layer between the ceramic paint coating and the metal wall to be protected, but which also functions as a protective material in combination with one or more silicon compounds.

There was prepared a paint in an aqueous liquid starting from a mixture of powders (finely ground with iron balls), of the following composition:

Paint no	SiC	Clay	B_4C	Cr + 10% Al precalcined in air atmosphere at 800°C
27	45% by weight	5% by weight	5% by weight	45% by weight

The paint was applied on a tubular cylinder of AISI-304 stainless steel, after a preliminary deposition of a connecting layer (0.05 mm) of chromium, applied by plasma-spray deposition in an argon atmosphere, followed by heat treatment in a furnace at 800°C, in an atmosphere of air, for one hour; whereafter there was carried out the carburation test described in example 1, with the only difference being a slightly shorter testing time (6 ½ hours). There was obtained the same positive result described in test 6 (absence of carbon black; refractoriness of the coating; unchanged plasticity of the base metal of the test piece).

Example No. 8:

This example is a variant of the preceeding one and aims at evidencing more clearly the refractoriness and protective capacity of chromium.

The paint used for this purpose had been prepared from a mixture of very finely dry-ground powder, by means of porcelain balls, starting from the following composition:

Paint no.	SiC	B_4C	Cr + 10% of Al precalcined at 800°C in air atmosphere
28	18% by weight	10% by weight	72% by weight

The paint, prepared in an organic silicone liquid, was applied on a small tubular cylinder of AISI-304 stainless steel, after deposition on it of a chromium connecting layer (0.05 mm) applied by plasma-spray in an argon atmosphere. The painted cylinder was then heat treated in a furnace at 800°C, in an air atmosphere, for one hour. This was followed by the carburation test, as described in example 1, except that the temperature was raised to 125°C, the gaseous mixture was humidified by bubbling it through water at room temperature, and that the duration of the test amounted to 6 and ½ hours.

There was obtained the same positive results as those described in test 6 (i.e.: absence of carbon black; refractoriness of the coating; unchanged plasticity of the base metal of the test piece).

Example No. 9:

This example is a modification of the preceeding one, aiming at proving that the chromium is capable of acting together with the silicon compound in developing a satisfactory protection also when it has not been pre-calcined with chromium.

The paint used in this case was prepared from a mixture of finely dry-ground powders by means of porcelain balls, starting from the following composition:

Paint no.	SiC	B_4C	Cr
29	18% by weight	10% by weight	72% by weight

The paint was prepared and applied as described in example 8. The carburation test was conducted as described in example 1, but with the difference that the duration amounted to 7 hours and a half instead of 7 hours. There was achieved the same positive results described in the preceding tests (examples nos. 6, 7 and 8).

Example No. 10:

This example intends to prove how the silicon compound may be different from the carbide or the nitride, or how it is possible to use a mixture of silicon compounds, or alternatively, how the silicone compound or compounds may be replaced by other ceramic compounds (e.g.: Al_2O_3 + 8% of Co, of B_4C + 10% of Al) and how iron or its oxide are important auxiliary components.

Ten different paints were prepared by dispersing in an organic silicone medium the finely ground powdery mixtures of the components, in the precentage ratios indicated in Table 3.

With these paints were painted 10 tubular cylindrical test pieces of AISI-304 stainless steel (ext. ∅ = 33 mm; int. ∅ = 29 mm; h = 25 mm), previously coated by deposition with a connection layer (0.05 mm) of chromium applied by a plasma-spray in an argon atmosphere, followed by a heat treatment in a furnace for 1 hour in an air atmosphere at 800°C.

Thereupon was carried out the carburation test, as described in example 1.

For the 10 painted tests samples there were obtained positive results, in everything similar to those obtained in the previous tests (examples: 6, 7, 8 and 9).

The best samples seem to be samples (33, 32 and 36) for their better looks, and for the resistance of the coatings formed by the corresponding paints, in comparison to the other paints which, at any rate, ensure definitely good results both with regard to the repulsion of the carbon black as well as to the refractoriness. The malleability of the metal has remained unchanged.

TABLE 3

Paint no	$ZrSiO_4$ % b.w.	Si_3N_4 % b.w.	SiC % b.w.	B_4C % b.w.	B_4C+10% Al pre-calcined at 800°C % b.w.	Al_2O_3+8% Co pre-calcined at 800°C % b.w.	Fe_2O_3 % b.w.	Remarks
30		85.7		9.5			4.8	
31			85.7	9.5			4.8	
32	40	20	20	20				
33	38	19	19	19			5.0	
34(*)			90	10				mixture ground with iron balls
35					45	50	5.0	
36	85				10		5.0	
37	90				10			
38			90		10			
39			80		20			

(*) The paint no. 34 was applied after the application of a "primer", consisting of a paint containing B_4C + 10% Al precalcined at 800°C.

Example No. 11:

A further cylindrical test piece of AISI-304 stainless steel (with extr. ∅ = 33 mm; intr. ∅ = 29 mm; h = 25 mm) was completely sand-blasted, whereupon onto its inner surface was spread, by plasma-spraying in an argon atmosphere, a layer of chromium (0.05 mm). Finally there was applied a paint consisting of Cr_2O_3 in a very fine powder dispersed in the organic silicone liquid (of example 2).

Onto the outer surface of the test piece was applied paint 13 of example 2.

The dried test piece was kept for 1 hour in a furnace at 800°C in air, and finally was subjected to the carburation test in the quartz-tube, according to the procedure described in example 1. The results of the test proved positive (i.e.: absence of carbon black on the coatings, refractoriness of the coating, unchanged plasticity of the metal material after the deformation crushing test).

Example No. 12:

Two tubular cylindrical test pieces of AISI-304 stainless steel (extra. ∅ = 33 mm; intr. ∅ = 29 mm; h = 25 mm) were completely sand-blasted, then subjected to coating with nickel-boron by chemical deposition with an electroless sodium boranate or sodium boronhydride process. After carrying out in the given order the operational steps 1, 2, 3, 4, 5 and 6 of the electroless technique, as indicated hereunder:

1) *Chemical cleaning*: by contact, first with a degreasing solution of NaOH at a concentration of 35% and then with a pickling solution of HCl at a concentration of 20%, inserting between the alkaline treatment and the acid treatment a thorough washing with water;

2) *A thorough washing with water*, followed by

3) *a sensitization* by dipping into a solution prepared by adding to 1 litre of water 125 cc of concentrated HCl and 25 g of $SnCl_2.2H_2O$;

4) *Thorough washing with water*;

5) *activation by dipping* into an acid solution prepared by adding to 3875 cc of distilled water 10 cc of concentrated HCl and 1 gram of palladium;

6) *Thorough washing with water*,

the process comprises the preparation of two solutions A and B of the following composition.

Solution A:	40 g of NaOH + 1 g of $NaBH_4$/litre	
Solution B:	$NiCl_2.\ 6H_2O$	30 g/litre
	ethylendiamine	50 g/litre
	Tl_2SO_4	0.07 g/litre

and the joining together of the solutions at 90°C, followed by the immersion or dipping therein of the metal article to be nickel coated.

The small test-piece cylinders were kept in this bath for 1 hour, whereafter they were extracted from it, wiped with filter paper, dried and finally painted, one with paint 12 and the other with paint 13 of the table of example 3, after which they were kept in a furnace for 1 hour at 800°C in an air atmosphere.

The test pieces were finally subjected to the carburation test in a quartz tube as described in example 1.

The results of the test were almost similar to those obtained in the test of example 11.

Example No. 13:

Two tubular cylindrical test pieces of AISI-304 stainless steel (extr. ∅ = 33 mm, intr. ∅ = 29 mm; h = 25 mm) were completely sand-blasted and then painted separately with respectively paint no. 12 and no. 13 of the table of example 3.

After remaining for a certain stretch of time in the furnace at 800°C, in an air atmosphere, the two test pieces were subjected to the carburation test in a quartz tube according to the procedures described in example 1.

The results of the test proved satisfactory. In fact, there was practically no carbon black, the refractoriness of the coatings was good, while the plasticity of the metal remained unchanged (as witnessed by the crushing test). The coatings formed by the paints were, however, found damaged by thermo-mechanical stresses, above all in the outer surface of the cylinders.

Example No. 14:

This example is given for providing the good adhesion properties of the protective coating paints on a tubular metal wall made of a high-temperature resisting alloy, known by the mark HK-10, and to illustrate the resistance of the protective coatings to the thermo-mechanical stresses caused by fast cooling.

A ring (extr. Ø 130 mm; intr. Ø 110 mm; h = 40 mm) obtained by slicing (cutting) from a tube of HK-10 alloy, was cut up into 4 (four) sections 1, 2, 3 and 4 (see the accompanying drawing).

The concave surfaces were treated in this way:

Section 1: just sand-blasted;

Section 2: sand-blasting followed by deposition of a chromium coating (0.05 mm) on the portion of arc R' at 1 cm from the left end of the section itself;

Section 3 : sand-blasting followed by deposition of a chromium coating (0.05 mm) on the portion of arc R" at 1 cm away from the right end of the section itself;

Section 4: sand-blasting followed by deposition of a chromium coating (0.05 mm) on the whole portion of arc R‴.

The deposition of the chromium coating was carried out by means of the plasma-spray technique in an argon atmosphere. The four sections, at this point, were welded together with Avesta 254 E electrodes (corresponding to AWS E 310-15 standards) by arc-welding after chamfering the ends of the sections, thereby achieving joints I, II, and III as indicated in the drawing.

The presence of the chromium coating at the opposite ends of joint III did not cause any difficulties in the welding operation and did not reduce the quality of the weld itself.

After completion of the weldings, on the surfaces corresponding to the arc portions R', R" and R‴ there was applied painting 13 of example 3, covering also the surfaces adjacent to joint II. The arc comprising the first section and half of the second section, bonded together by joint I, was left simply sanded.

The sample thus prepared was, at this point, introduced into a furnace at 900°C in an air atmosphere, in which it was kept for 600 hours.

It was then removed from the furnace and subjected to a fast cooling under a cool air impelling hood (cooling time at 50°C; 8 minutes).

At this point it was noted that:

- the unprotected area of section 1 and part of the area of section 2 showed a blue tinge due to the oxidation suffered;
- the coating generated by the paint had come off only from the surfaces adjacent to joint II, which had not been treated with the intermediate chromium coating;
- all the remaining surfaces proved protected by the coating which showed excellent adhesion, coherence and refractoriness characteristics.

Example No. 15:

An HK-40 steel tube (extr. Ø 130 mm; intr. Ø 110 mm; 1 = 1300 mm) fitted at one end with a flange and counter-flange provided with a central pipe for the feeding of gases (intr. Ø 10 mm, extr. Ø = 13 mm), and at the other end provided with a disc welded onto it and carrying at its centre a gas outlet pipe, after undergoing sand-blasting of the whole inner surface, coating with a chromium layer (0.05 mm) by plasma-spray deposition in an argon atmosphere, and after a final coating with paint no. 13 of example 3, was placed into a furnace at a temperature stabilized at 1000°C. For the first two hours the gas inlet and discharge pipes in the tube were kept in free communication with the surrounding air. Subsequently, the tube was kept under carburation conditions (in the presence of a gaseous mixture consisting of: 34% by vol. of CH_4, 14% by vol. of CO, 52% by vol. of H_2 at a feed rate of 75 lt/hr), alternated by oxidation conditions (in the presence of humidified air at room temperature by bubbling through a suitable vessel) until totalling an overall operational period of 1435 hours. This period consisted of 44 carburation cycles (for a total of 391 hours), each of which was alternated by a carburation cycle (until totalling 44 oxidation cycles for a total of 1044 hours). During this operational period, because of a series of sudden breakdowns in power supply, the furnace temperature dropped twice to 450°C, then a third time to 580°C and a fourth time to 500°C. The tube, observed with the flange opened, at the end of the test was found in excellent condition. For a more severe examination, the tube was cut into 14 crop ends of equal length. This allowed one to ascertain that the chromium coating, superficially vitrified by the ceramic paint, was found metallurgically anchored to the HK-40 metal wall.

Example No. 16:

The seventh annular crop end of the preceding example (starting from the flange of the tube of the preceding test) was sliced along a generating line; then, by heating to bright red with an oxyacetylene torch the opposite zone of the generating line, the annular crop end was then reshaped by means of plastic heat creep so as to acquire the shape of the letter ω wherein the central crest or peak shows a bending radius of 1.2 cm. On the top of the crest there had formed some cracks, some 1 - 1.5 mm deep.

A similar test was carried out on a crop end of virgin HK-40. In this case much deeper cracks (of 3 - 4.5 mm) were formed. Evidently, the metallurgical diffusion of the chromium coating improves the mechanical properties of the HK-40 alloy which, in as much as a material produced by centrifugal casting, notoriously shows a crystallite structure with a columnary orientation.

Example No. 17:

An HK-40 steel tube (extr. ∅=130 mm; intr. ∅ = 110 mm; 1 = 1300 mm) with open ends was subjected to the protective treatment according to that described in example 15. After baking at 900°C in an atmosphere of air, for a period of 3 hours, was inserted by welding into the coil of an industrial cracking furnace for the production of ethylene from "virgin naphta". This product is defined by the following characteristics:

density (max. at 60°F) =		730 kg/cu/mt.
initial boiling point (min.) =		35°C
max. evaporate :		50% at 125°C
max. evaporate :		95% at 180°C
max. final boiling point:	at	190°C
min. content of sulphur:		50 p.p.m.

The tube has been operating for about 5 months, and at a pyrometric observation shows a regular behaviour. The test is still going on.

WHAT WE CLAIM IS:

1. A process for the protection of ferrous and non-ferrous metal surfaces against corrosion by carburation at high temperatures and corrosion by oxidation, the process comprising : preparing a binary or polynary mixture of fine powdered product having a particle size from 0.04 to 0.00004 mm, the mixture comprising at least one first component selected from Si, Si_3N_4, $ZrSiO_4$, SiC, SiO_2, glass, clay, Fe-Si, Al_2O_3, ZrO_2, MgO, WO_3, Cr_2O_3, Cr_3C_2 and Cr, the or each said first component being present in an amount of from 0.5 to 92% by weight, and the total amount of the said first components not exceeding 99.5% by weight, and from 0.5 to 50% by weight of at least one second component selected from AlB_2, AlB_{12}, Al-stearate, Al, Cr-Al, B_2O_3, B_4C, Fe_2O_3, TiB_2, ZrB_2, Fe and Fe-Cr; dispersing the said mixture in a liquid medium acting as a binder, in such a quantity as to obtain a composition suitable for painting of the desired density, the said liquid medium being an aqueous or an organic liquid; mechanically homogenizing the composition, and then painting or coating a metal surface of a product to be protected, the surface having been preliminarily sand-blasted or chemically cleaned; drying the coated product, first in the air at room temperature, and then at a temperature higher than room temperature; and finally baking the coating at a temperature not lower than 700°C in an oxidizing atmosphere.

2. A process as claimed in Claim 1, wherein the said organic liquid medium consists of 50 - 86% by weight of at least one aromatic solvent and 50 - 14% by weight of a silicone with a molecular weight of from 1300 to 3600, the said silicone being soluble in the organic aromatic solvent.

3. A process as claimed in Claim 2, wherein the silicone has a silicon content of 14 to 37% by weight.

4. A process as claimed in any of Claims 1 to 3, wherein on the metal surface, before painting and after sandblasting or chemical cleaning, there is deposited by plasma spray deposition a metal chromium coating acting as a thermoresistant anchoring layer.

5. A process as claimed in any of Claims 1 to 3, wherein on the metal surface, before painting and after sandblasting or chemical cleaning, a nickel-boron coating acting as an anchoring thermoresistant layer is deposited by electroless sodium boranate process.

6. A process as claimed in any of Claims 1 to 5, used to protect the inside surfaces of tubes or metal products subject to carburation corrosion in consequence of operational conditions in which carbon black at a high temperature is produced.

7. A process as claimed in any of Claims 1 to 5, used to hinder or at least reduce the formation of coke in reactor tubes of hydrocarbon cracking furnaces for the production of olefins.

8. A process according to Claim 1 for the protection of ferrous and non-ferrous metal surfaces against corrosion by carburation at high temperatures and corrosion by oxidation, carried out substantially according to the painting process disclosed in any of Examples 3 to 17.

9. An article having metal surfaces protected by the process as claimed in any preceding claim.

10. A coating composition for protecting ferrous and non-ferrous metal surfaces against corrosion by carburation at high temperatures and corrosion by oxidation, the composition comprising: a binary or polynary mixture of fine powdered product having a particle size from 0.04 to 0.0004 mm, the mixture comprising at least one first component selected from Si, Si_3N_4, $ZrSiO_4$, SiC, SiO_2, glass, clay, Fe-Si, Al_2O_3, ZrO_2, MgO, WO_3, Cr_2O_3, Cr_3C_2 and Cr, the or each said first component being present in an amount of from 0.5 to 92% by weight, and the total amount of the said first components not exceeding 99.5% by weight, and from 0.5 to 50% by weight of at least one second component selected from AlB_2, AlB_{12}, Al-stearate, Al, Cr-Al, B_2O_3, B_4C, Fe_2O_3, TiB_2, ZrB_2, Fe and Fe-Cr; the mixture being dispersed in a liquid medium acting as a binder so as to obtain a composition suitable for painting, the said liquid medium being an aqueous or an organic liquid.

11. A composition as claimed in Claim 10, wherein the said organic liquid medium consists of 50 - 86% by weight of at least one aromatic solvent and 50 - 14% by weight of a silicone with a molecular weight of from 1300 to 3600, the said silicone being soluble in the organic aromatic solvent.

12. A coating composition according to Claim 10, substantially as herein described with reference to any of paints 1 to 39 disclosed in the Examples and Tables.

MARKS & CLERK

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1 SHEET *This drawing is a reproduction of the Original on a reduced scale*